Supporting Information

Ultrafast Elemental and Oxidation-state Mapping of Hematite by 4D Electron Microscopy

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A. **PINEM-electron effect on the broadening of the core-loss edge (PINEM stands for photo-induced near-field electron microscopy)**

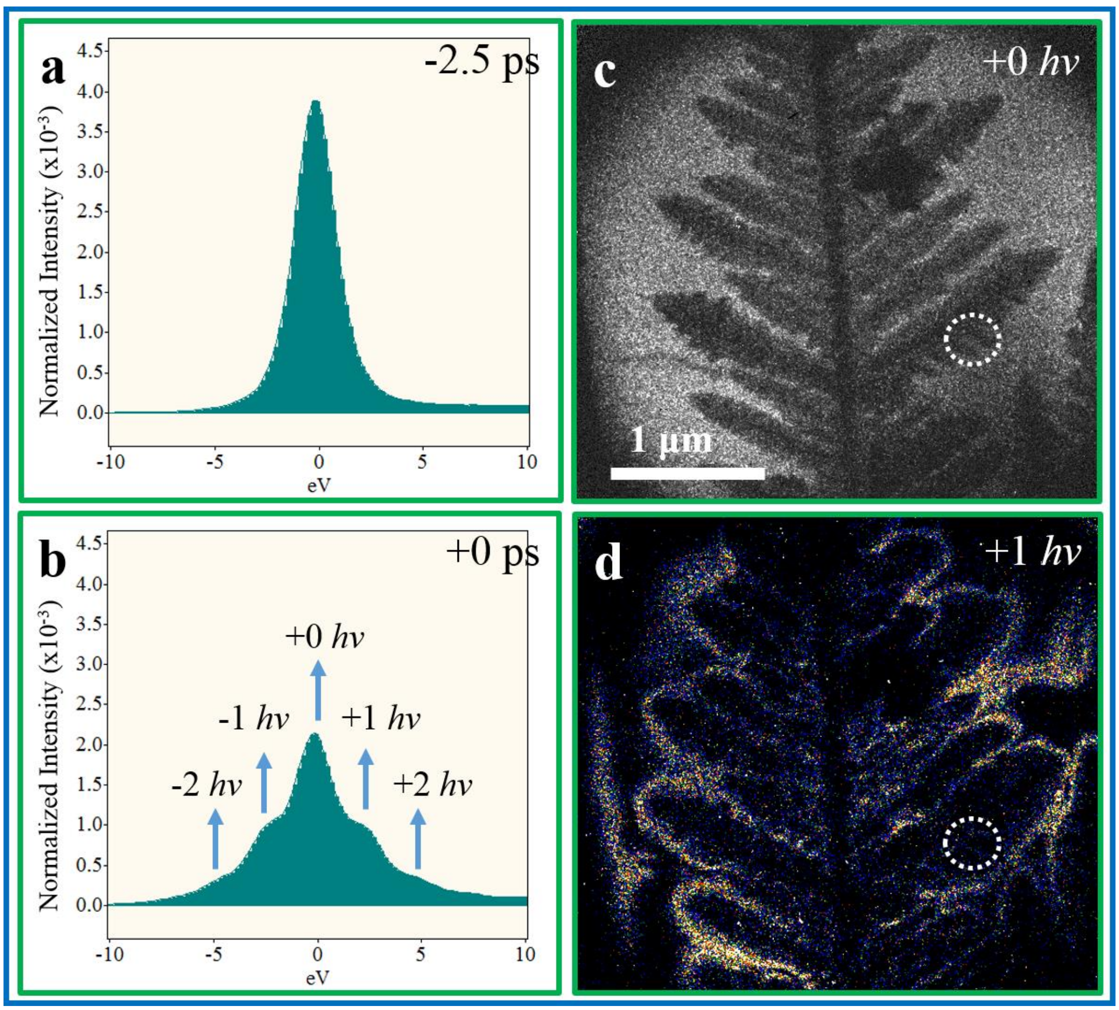

Figure S1. (**a**) Zero-loss EELS spectrum at negative time before excitation. (**b**) PINEM-electron effect on the zero-loss spectrum at 0 ps. (**c**) Ultrafast TEM image using zero-loss electrons. (**d**) PINEM image using electrons gaining single photon energy at 0 ps. A 2 eV energy slit was used to select electrons to create images in **c** and **d**, and the circled area is typical probing area.

Compared with Fig. S1a, the zero-loss spectrum in Fig. S1b shows significant broadening due to the energy exchange between the electrons and photons overlapped in time, which is the so-called PINEM-electron effect.[1] Fig. S1c shows the ultrafast TEM image of particle using zero-loss electrons without exchanging energy with photons, while Fig. S1d shows the PINEM image of particle using electrons gaining a single photon energy. The circled area is a typical probing area, covering haematite particle with a blank gap. Since the ratio of PINEM-electrons to probing electrons decreases away from the edge of the haematite particle to both sides,[2] and the width of the particle is obviously larger than the blank gap, the average ratio of PINEM-electrons to probing electrons in the blank gap area should be stronger than that on the haematite. All the PINEM-electrons contribute to the broadening of the zero-loss spectra, while only the electrons passing through the haematite contribute to the Fe L_3-edge. Thus the model based deconvolution method assuming that 100% of the PINEM-electrons causes the broadening of Fe L_3-edge as shown in Fig. 3c might lead to a calculated intrinsic broadening slightly smaller than the actual value.

B. Ultrafast iron oxidation-state and elemental mapping

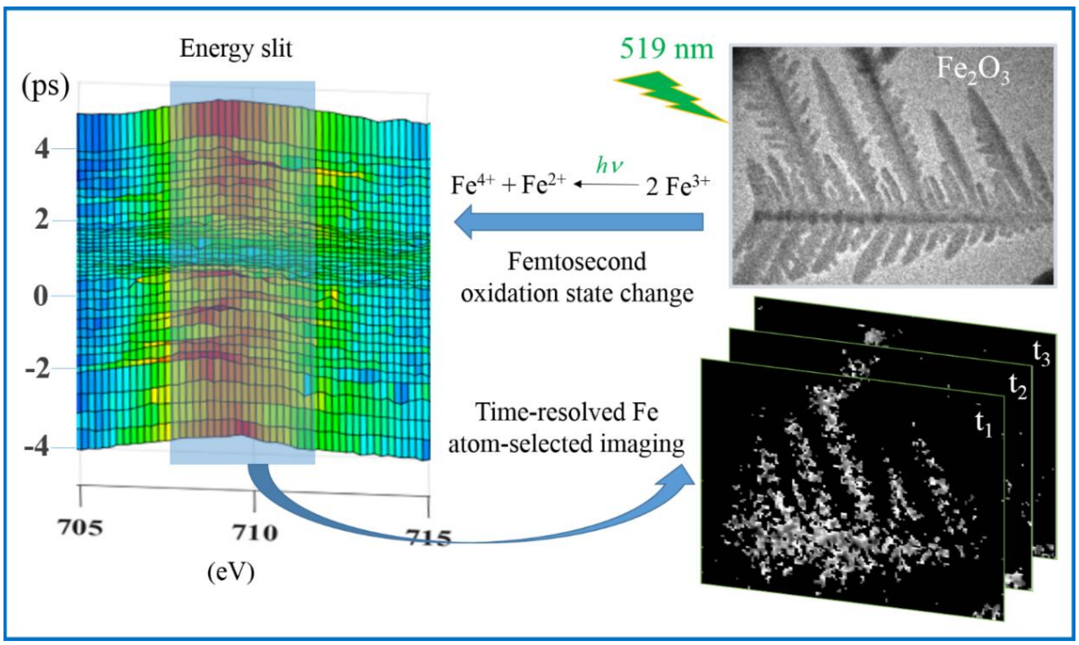

Figure S2. After the 519 nm laser pulse excitation, part of the Fe^{3+} ions were converted to Fe^{2+} and Fe^{4+} ions, leading to the broadening and lowering, and subsequent recovery of the Fe L_3-edge in EELS. Such dynamics were also reflected in the corresponding ultrafast elemental mapping, using a narrow window of 4 eV.

References

1. Barwick, B.; Flannigan, D. J.; Zewail, A. H. *Nature* **2009**, *462*, 902–906.

2. Park, S. T.; Lin, M. L.; Zewail, A. H. *New J. Phys.* **2010**, *12*, 123028.